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Research Synthesis and Characterization of 2D Conjugated Polymers

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Fredrico Rosei

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
INRS Energie Materiaux Telecommunications Varwnnes (Canada)
1650 Blvd. Lionel Boulet
Varennes QC J3X1S2 Canada

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
USAF/AFRL
AFOSR
875 North Randolph Street
Arlington VA 22203

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

Use heterocyclic multidentate monomers specifically designed for this purpose by Density Functional Theory calculations. The main challenge in this design is the geometry of the monomer and the resulting olgiomer (i.e., the most favorable all-trans geometry of a polythiophene chain on the Scheme should necessarily result in a continuous brick wall 2D structure). Furthermore, the design should eliminate any steric hindrances in the oligomers which would result in non-planar conformations.

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15. SUBJECT TERMS

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ANNUAL PROGRESS SUMMARY
To: technicalreports@afosr.af.mil
Subject: Annual Progress Statement to (your AFOSR Program Manager)
Contract/Grant Title:
Contract/Grant #: FA9550-06-1-0325
06IU008

Reporting Period: July 2006 to June 2007
Annual accomplishments (200 words max):

The objective of the first year of our project was to demonstrate the feasibility of synthesis of conjugated polymers by surface-confined polymerization.
We have focused on model building blocks which are structurally relevant to those that we intend on using for 2D polymerization, yet polymerize in 1D fashion, which simplifies the control of the reaction and the analysis of its final products.
Three independent approaches to polymerization were considered:
1. catalytic polymerization (surface template acting as a catalyst);
2. electrochemical polymerization;
3. topological 1,4-addition polymerization.

While there were a few examples in the literature for approaches 2 and 3, our polymerization approach using catalytic coupling (Ullmann reaction) on flat metal surfaces (Cu) is completely new. Within the constraints of funding awarded by AFOSR, we decided to place the main emphasis to this latter approach (1). We have found that depositing di-iodinated aromatic molecules on the surface of atomically flat copper under Ultra High Vacuum (UHV) conditions yields lines of conjugated polymers. The most successful experimental runs were performed on Cu(110), exploiting the anisotropy of this surface. The method appears to be rather general and the polymer lines can obtained from different monomers (from diiodobenzene, to yield polyphenylene (PPP) from di-iodoethylenedioxythiophene to yield poly(ethylenedioxy)thiophene PEDOT). PPP lines running along the closed packed direction are displayed in Figure 1 (a), whereas PEDOT lines are shown in Figure 1 (b).

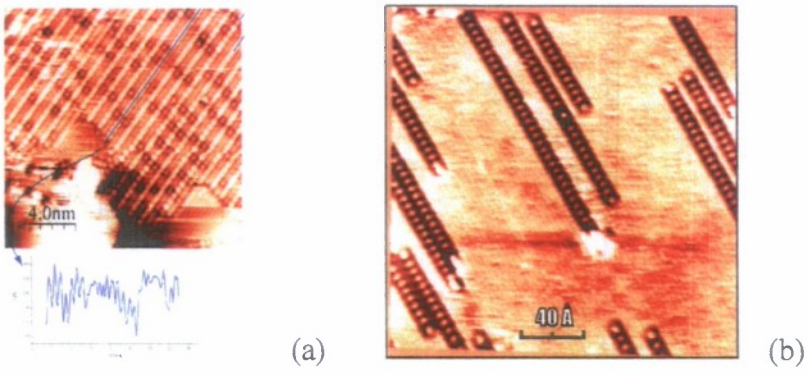

Figure 1. (a) STM image of PPP 'lines' running along the [1-10] direction on Cu(110), obtained by reaction di-iodobenzene on this surface. The dots in between the lines are Iodine atoms. (b) STM image of PEDOT lines obtained by depositing di-iodo-edot molecules on this surface.

Although the initial breaking of C-I bonds occurs well below room temperature (typically at 180 K), an increased temperature (473 K, either during growth or as post-deposition annealing) is required to achieve high degree of polymerization and ordering of the polymer lines on the surface.
At these higher temperatures, PEDOT and PPP polymers orient along the close packed direction of the surface (namely, the [1-10] direction).
We also established that the reaction byproduct (copper iodide) creates separate phases on the surface with the characteristic 2×2 reconstruction that is known to occur when depositing atomic I on Cu(110). This phase segregation is displayed in Figure 2.

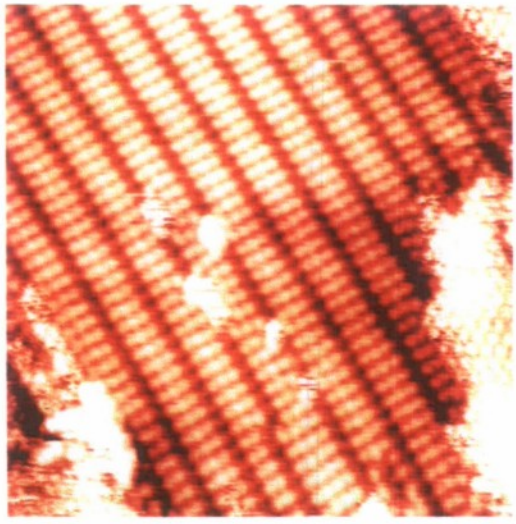

Figure 2. STM image of PEDOT formed by Ulmann coupling of di-iodo-edot on Cu(110). Also visible are areas (e.g. on the right side of the micrograph) are CuI areas, which can be recognized by the characteristic c(2×2) reconstruction.

These copper iodide phases are inert to the monomer. Thus, complete coverage of the surface with the polymer cannot be achieved under these conditions. In future work, we intend to overcome this obstacle by designing 2D polymeric structure with pores which could accommodate this byproduct.
Further characterization by Infrared Spectroscopy, X-Ray Photoelectron Spectroscopy and Ultraviolet Photoelectron Spectroscopy are under way.
We have also conducted preliminary experiments on the two other low index surfaces of copper, namely Cu(001) and Cu(111). It is apparent that the polymerization on these surfaces is not nearly very effective and yields significantly disordered materials, probably because in the case of Cu(110) the surface's anisotropy guides the formation of polymer lines along the preferential direction of the substrate.

Archival publications (published) during reporting period:

D.F. Perepichka and F. Rosei, *Angew. Chem.* Int. Ed. **46**, in press (2007).

Two manuscripts (one on PPP and the other on PEDOT) are currently in preparation.

Changes in research objectives, if any: No significant changes so far.

Change in AFOSR program manager, if any:
Our initial program manager was Dr. Ken Goretta. He was replaced by Dr. James Fillerup, who was himself replaced by Dr. Julie Moses (who is our present program manager).

Extensions granted or milestones slipped, if any:

The project was recently renewed for funding for a second year with partial funding from the AFRL and from AOARD.

SAMPLE ANNUAL PROGRESS SUMMARY (typical)
To: technicalreports@afosr.af.mil
Subject: Annual Progress Statement to Dr. Robert Barker
Contract/Grant Title: A Plasma-Assisted Megawatt Class Microwave Source with an Output of 1 KJ per Pulse
Contract/Grant #: FA9550-05-1-0292
Reporting Period: 1 July 2004 to 30 June 2005
Annual accomplishments (200 words max):
The UMD helix Pasotron demonstrated peak power levels of 1.8 MW, long pulse (~600 usec) operation free from pulse shortening and breakdown, and 600 J of microwave energy output per pulse. Studies of the voltage and current scaling laws of the helix Pasotron indicate that it will be possible to extend the output energy to 1.2 kJ per pulse and beyond.
Archival publications (published) during reporting period:
1) G. S. Nusinovich, Y. Carmel, A. G. Shkvarunets, J. C. Rodgers, T. M. Antonsen, Jr., V. L. Granatstein, Y. P. Bliokh, D. M. Goebel, and J. P. Verboncoeur, "The Pasotron: Progress in the Theory and Experiments," *IEEE Trans. Plasma Sci.* **52**, 845, 2005.
2) G. S. Nusinovich and O. V. Sinitsyn, "Effect of transverse nonuniformity of the rf field on the efficiency of microwave sources driven by linear electron beams," *Phys. Plasmas* **12**, 093107, 2005.
Changes in research objectives, if any: None
Change in AFOSR program manager, if any: None
Extensions granted or milestones slipped, if any: None